

CRYSTALLISATION OF COAL ASH MELTS

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The formation of ash deposits within p.f. coal-fired boilers may cause severe reduction in heat transfer and thermal efficiency. These deposits vary in nature from friable, slightly sintered fouling to dense, semi-vitreous slags. Utility boiler designers and operators use a variety of methods (9) to ascertain various design criteria or the likelihood of the ash to form deposits (its slagging or fouling propensity). The major technique used is the standard ash fusion test (2) in which a cone or pyramid of coal ash is heated at a given rate, both in air and a mildly reducing atmosphere, while the temperatures at which various degrees of deformation occur are recorded. This method is known to give inaccurate indications of slagging propensity due mainly to the subjective nature of the test and the fact that the technique does not duplicate the thermal history experienced by coal matter in a p.f. boiler.

Various laboratory studies, (5,6) have shown that significant fusion of coal mineral matter, the precursor to ash, occurs within a very short time-frame at temperatures analogous to those in the combustion zone of a boiler (about 1550-1650°C). This is confirmed by microscopical studies of p.f. fly ash. Despite total flight times of about 2s (6) and a temperature gradient ranging from 1650°C to about 300°C the characteristic nature of fly ash, that of hollow cenospheres is due to the presence of significant liquid phase at some stage of the particles' histories. This is further confirmed by mineralogical studies of the particles which sometimes reveals the presence of a refractory phase which had crystallised from a liquid and was not the product of thermal decomposition of an individual coal mineral (4,6). Raask has shown that the growth of deposits is by initial adhesion of fly ash particles to the surface of deposits already present. This adhesion is due to the liquid phase present and the rate of assimilation of the captured particle will be by sintering by viscous flow. From the theory of sintering (6) the rate of increase in strength (s) i.e. growth, of the deposit is given by:

$$\frac{ds}{dt} = \frac{3\gamma k}{2\eta r}$$

Where γ is the surface tension coefficient of the viscous phase, k a constant, r the initial radius of the particles and η the viscosity of the liquid. It can be seen that the nature of a deposit can be described by the degree of sintering which has taken place. For a given coal ash the parameters r and γ are effectively constant with respect to the variability of the viscosity. Therefore the factors which affect the rheological behaviour will determine to a great extent the rate of growth by viscous flow. For homogeneous melts the determining factors are temperature and chemical composition. Lauf has observed that the amount of fly ash particles collected at the outlet of various boilers was inversely proportional to the calculated viscosity (taking account of the different ash contents between the parent coals). (4) The viscosity was calculated by two methods based on the chemical composition; those of Watt and Fereday and Reid. (7,8) The observations confirm the viscosity relation above, albeit qualitatively and the assumption of complete melting of the coal mineral matter. A factor which has not received attention in the literature is the crystallisation of ash particles and/or the deposits already present. With devitrification of a phase from homogeneous melt the composition of the liquid phase will change depending on the precipitating phase and the degree of crystallisation. This in turn will directly affect the viscosity and hence the rate of growth of the deposits.

subjected to a series of crystallisation treatments within the reducing atmosphere. The quenched samples were analysed for phases present by X-ray diffraction and for the ratio of ferrous to ferric iron by a wet chemical technique.

The major observation of the crystallisation study of the ash melts was that the phase or phases which were precipitated contained only the predominant components, the minor components remaining in the liquid phase. Another observation was the reluctance of the melt to crystallise to the expected number of phases; only anorthite ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) was determined to crystallise for the two western type ashes and mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) as the primary phase with a secondary phase of iron spinel; a member of the solid solution series magnetite ($\text{FeO} \cdot \text{Fe}_2\text{O}_3$) - hercynite ($\text{FeO} \cdot \text{Al}_2\text{O}_3$), only for the eastern type ash.

The crystallisation of the ternary compositions is discussed with respect to that predicted for each from the phase diagram for the system. The normalized ternary compositions of the two western type ashes were plotted on the phase diagram and the observed crystallisation compared with that predicted from the diagram and the behaviour of the model compositions. The system was found not to be able to correctly predict the primary crystalline phase for one of the two ashes but could account for the crystallisation of anorthite only for the other ash.

As quaternary systems are quite complex both the representation and crystallisation of compositions are discussed in the presentation. Planes of constant MgO content was used as the method of representation of the $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$, with planes at 5, 10 and 15 wt% prepared from literature sources and results of this study (3). The observed crystallisation of the glasses studied is discussed in terms of the equilibrium system, a striking observation being the apparent low solubility of magnesia in the compositions studied; a magnesia bearing phase precipitating for nearly all the glasses as primary or secondary phase. The corresponding normalised composition of the western type ashes were plotted on the 5% plane and the observed behaviour compared with the predicted crystallisation behaviour. As with the ternary system the four-component system only correctly predicted the primary crystalline phase for one of the ashes. Also the system would predict that a secondary phase containing magnesia would be expected to crystallise; behaviour which was not observed.

The true representation of the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-iron oxide}$ is as a quinary system which is too complex for normal analysis. The results of the ferrous to ferric ratio of the quenched samples showed significant amount of ferric iron present. Fortunately analysis of the crystalline phases shows that predominantly the ferrous iron is taken up by the iron bearing phase (there was some evidence of solid solution of ferric iron in the iron spinel phase) and therefore the system could be approximated by the quaternary system $\text{CaO-FeO-Al}_2\text{O}_3\text{-SiO}_2$. Planes of constant FeO content (5-30 wt% at 5% increments) have been prepared from literature sources and the results of the crystallisation studies of the glasses are discussed in terms of the system. Unlike the quaternary system above the iron oxide remains in solution compared with magnesia. This would be predicted from the planes of the system and was observed in the crystallisation studies; no primary phase containing iron oxide was determined even for the glasses containing 20 wt% equivalent FeO. The corresponding normalised composition of the three ashes (iron oxide expressed as equivalent FeO) was plotted on the relevant plane of the system and the observed behaviour compared with that predicted from the phase diagram and the behaviour of the model compositions. The system correctly predicted the primary crystalline phase for all the ashes and could account for the crystallisation of anorthite only for the two western type ashes. While initially the system could not predict the crystallisation of iron spinel as the secondary phase for the eastern type ash analysis of the

Thus it will be of great value to be able to predict to some extent the crystallisation behaviour of coal ash melts. For simplicity it is initially necessary to consider that the crystallisation will be from a homogeneous melt. The data obtained can be extended to the phenomena of boiler deposits by using an accurate model of viscosity of ash melts based on chemical composition. The main aim of the study presented here was to obtain relevant crystallisation data of coal ashes and to model the behaviour so as to be able to predict the devitrification of a given ash. Coal ash is usually described as a mixture of up to 11 oxide components and though various investigators (1) have attempted to simplify the system by using certain equivalences the authors have chosen to use the major three or four components to model the observed behaviour.

For eastern type coal ashes the major components are silica, alumina, iron oxide and lime, whereas for western type ashes the major components are silica, alumina, lime and iron oxide or magnesia. In both cases these may comprise 90 wt% or more of the total composition of the ash. Sanyal and Williamson have shown that the initial crystallisation of two western type ashes of low iron oxide content (5% or less) could be described by the normalised composition on the ternary equilibrium diagram of the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$. The study presented here has extended the investigation to the devitrification of eastern type ash as well as two western type ashes and the crystallisation of model compositions corresponding to the normalised compositions of coal ashes. The systems studied were; $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$, $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ and $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-iron oxide}$, to ascertain which system or systems govern the behaviour most adequately.

The crystallisation of three coal ashes (two western and one eastern type) was determined under laboratory conditions by fusing a sample in an electric muffle furnace to achieve complete melting of the coal minerals. Devitrification was induced by reducing the temperature to a given level and leaving the sample for a given time. The sample was then quenched, effectively freezing the phases present at the elevated temperatures. The sample was analysed by petrographic microscopy and X-ray diffraction. The treatment was repeated over a range of temperatures and times for each sample.

For the study of the crystallisation of the model compositions five ternary CaO , Al_2O_3 and SiO_2 compositions were chosen which were expected to exhibit different behaviour (from the corresponding phase diagram) while being in the compositional region relevant to coal ashes. Homogenous glasses were produced by fusing the correct mixture of the oxide components. The crystallisation of the glasses was determined in an analogous manner to that used for the ash melts. The same five compositions were used as the basis for the study of the crystallisation of the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$. Two series of compositions were prepared based on the ternary compositions with 5 and 10 wt% MgO respectively. Glasses were produced and the liquidus and crystallisation behaviour determined by a quenching technique.

As iron oxide exists in two oxidation states (ferrous and ferric) in p.f. ash deposits it was necessary to study the crystallisation of glasses in the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-iron oxide}$ in a controlled atmosphere; the same as that used in the reducing part of the standard ash fusion test i.e. $\text{CO}_2\text{:H}_2$ mixture 1:1 v/v. The range of iron oxide content in coal ashes is wider than that of magnesia and hence glasses were prepared with up to 20 wt% equivalent FeO . Two series of glasses were produced based on the five ternary compositions with 5 and 10 wt% equivalent FeO with another two series of glasses based on three of the five composition with 15 and 20 wt% equivalent FeO . The glasses were ground to a fine powder and each was

results of the model compositions indicated that ferric iron present in the liquid phase reduced the solubility of iron oxide which could account for the behaviour.

CONCLUSIONS

Therefore the system $\text{CaO-FeO-Al}_2\text{O}_3\text{-SiO}_2$, governs the initial crystallisation of the ash melts studied. The major aim of this study was to be able to predict the crystallisation of ash melts and relate the behaviour to boiler deposit growth. The phases present in six boiler deposits are compared with that predicted from the corresponding normalised composition in the presentation and shows that for all six (three western and three eastern type) the quaternary system predicts the primary phase. Furthermore the change in composition of the liquid phase for two of the ashes (one slagging the other non-slagging) for a range of degrees of crystallisation shows a great difference in terms of the relative concentration of the components which govern viscosity. While the liquid phase for the non-slagging ash became enriched predominantly in silica (the major viscosity-increasing component) the slagging ash became enriched in viscosity reducing components. This relates directly to the model of deposit growth discussed above and is a confirmation of the model.

The results of the study presented indicate the use of phase equilibria data to be phenomena of p.f. boiler deposits and the possible extension to the prediction of boiler fouling and slagging.

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